



# The resourcefulness of p(4-VP) cryogels as template for in situ nanoparticle preparation of various metals and their use in H<sub>2</sub> production, nitro compound reduction and dye degradation

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## ABSTRACT

Poly(4-vinylpyridine) (p(4-VP)) cryogels were synthesized under cryogenic conditions ( $T = -18^\circ\text{C}$ ) and were converted to positively charged forms by modifying with different alkyl dihalides of variable chain lengths such as 1,2-dibromoethane (1,2 BE), 1,4-dibromobutane (1,4 BB), 1,6-dibromohexane (1,6 BH), and 1,8-dibromooctane (1,8 BO). The chemical structure of synthesized supermacroporous 1,4 BB-p(4-VP) cryogels were confirmed by FT-IR spectroscopy. The 1,4 BB modified-poly(4-vinylpyridine) (1,4 BB-p(4-VP)) cryogels were used as template for in situ metal nanoparticle preparation as 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, and Fe) using chloride salts of Co, Ni, Cu, and Fe in ethanol. These metal-nanoparticle macroporous cryogel composites were employed in H<sub>2</sub> generation from hydrolysis of sodium borohydride (NaBH<sub>4</sub>). Metal nanoparticles embedded 1,4 BB-p(4-VP)-M were visualized by TEM, and thermal behavior of 1,4 BB-p(4-VP) cryogels were done by thermogravimetric analyzer (TGA). The metal content of 1,4 BB-p(4-VP)-M was estimated via atomic absorption spectroscopy (AAS). Multiple metal salt loading and reduction cycles were performed for 1,4 BB-p(4-VP) cryogels to increase the amount of contained Co. The activation energies, enthalpy, and entropy for NaBH<sub>4</sub> hydrolysis catalyzed by 1,4 BB-p(4-VP)-Co cryogel composites were determined as 47.6 kJ (mol)<sup>-1</sup>, 46.2 kJ (mol K)<sup>-1</sup>, and -146.9 J (mol K)<sup>-1</sup>, respectively. The cryogel network embedded with Co, Ni, Cu, and Fe nanoparticles was also used as a catalyst in the reduction of 4-nitrophenol (4-NP) in an aqueous solution in excess amount of NaBH<sub>4</sub>. Furthermore, the Cu metal nanoparticle-containing 1,4 BB-p(4-VP) cryogel was utilized in the degradation of methylene blue (MB).

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## 1. Introduction

Polymeric cryogels are macroporous hydrophilic and sponge-like hydrogels prepared under cryogenic conditions, i.e. below the freezing-point of the solvent, and a storage-thawing process [1,2]. The cryogels have unique chemical, physical and morphological properties such as super and interconnected pores, high porosity, better mechanical and chemical stability, modifiable chemical functional groups, and so on [3]. The applications of cryogels vary from biotechnology, energy and the environment [4–6].

The consumption of renewable energy has paramount significance to prevent environmentally damaging effects such as

green-house gas emissions, and emission of gases from burning of fossil fuels [7,8]. Hydrogen is assumed to be one of the most important renewable energy carriers. Therefore, many investigators have focused on the production of H<sub>2</sub> from the hydrolysis of metal and metal hydrides such as LiAlH<sub>4</sub>, MgH<sub>2</sub>, NH<sub>3</sub>BH<sub>3</sub>, or NaBH<sub>4</sub> catalyzed by Co, Ni, Cu, Fe, Ru, etc., nanoparticles [9,10]. Amongst these chemical hydrides, NaBH<sub>4</sub> has high storage capacity and ready production of hydrogen from its aqueous solution [10,11].

Nitrophenols (NP) are amongst the most common organic pollutants and they exist in many industrial and environmental wastewaters including those released from processes involving cosmetics, dyes, petrochemicals, photographic chemicals, etc. [12–14]. A range of different processes have been developed and investigated to remove, eliminate and/or reduce environmentally toxic compounds such as 4-NP. The methods most commonly used are electrochemical treatment, photocatalytic degradation, and so on [15,16]. To reduce the hazardous effects of nitro-aromatic

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compounds, they are generally converted to their amine forms that are considered more environmental friendly, and have some economical value for use in pharmaceuticals [17–19].

Wastewaters produced by textile industries have caused serious environmental concerns because they constitute non-stable azo dyes, and aromatic amino compounds that pose great hazards, are toxic, and dark colored [20,21]. Synthetic dyes such as methylene blue (MB) have complex aromatic structure and stability [22]. Therefore, biological methods are inadequate to decolorize synthetic dyes such as MB [23]. Fortunately, metal nanoparticles can be utilized for degradation of organic dyes such as methylene blue and eosin Y [24].

In this study, we report the preparation of p(4-VP) cryogels and their modification with various dibromo compounds to be used for in situ metal nanoparticle preparation. Then 1,4-BB-p(4-VP)-M (Co, Ni, Cu, and Fe) cryogel composites were used in various catalytic applications; in green energy carrier production by  $H_2$  generation from the hydrolysis of  $NaBH_4$ , and in the reduction of 4-NP, and then in the degradation of MB.

## 2. Experimental

### 2.1. Materials

4-Vinylpyridine (4-VP, 95%, Aldrich) as monomer, poly(ethylene glycol) diacrylate p(EGDA) (MW = 700 g/mol, Aldrich) as crosslinker, potassium persulfate (KPS, 99%, Sigma–Aldrich) as initiator, and N,N,N',N'-tetramethylethylenediamine (TEMED, Merck, 99%) as an accelerator were used in p(4-VP) cryogel preparation. The chemicals 1,2-dibromoethane (1,2 BE, Merck,  $\geq 99\%$ ), 1,4-dibromobutane (1,4 BB, Merck,  $\geq 98\%$ ), 1,6-dibromohexane (1,6 BH, Aldrich, 96%), and 1,8-dibromooctane (1,8 BO, Aldrich, 98%) were used as modifying agents. Sodium borohydride ( $NaBH_4$ , Merck, 98%) as reduction agent, and cobalt (II) chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ , Sigma–Aldrich, 99%), nickel (II) chloride hexahydrate ( $NiCl_2 \cdot 6H_2O$ , Riedel-de Haën, 97%), copper chloride ( $CuCl_2$ , Acros, 99%), and iron (III) chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ , Acros) were used as metal ion sources. 4-nitrophenol (Acros, 99%) was used. All the reagents and solvents (acetone and ethanol) were of analytical grade or highest purity available, and used without further purification. Distilled water (Millipore Direct-Q3 UV) was used throughout the experiments.

### 2.2. Synthesis of p(4-VP) cryogels

The synthesis of p(4-VP) cryogels was by cryogellation via free radical polymerization technique under freezing conditions. In brief, 0.6 ml (5.286 mmol) 4-VP, and 0.249 ml (7.53 mole % based on 4-VP) p(EGDA) were mixed in 7 ml DI water and 50  $\mu$ l TEMED was added, then vortex mixed to form a homogenous mixture, and the mixture was cooled in an ice bath for ten min. The initiator, 0.8 ml of KPS solution (1.66 mole % based on 4-VP) was included in the cryogel precursor and mixed until a homogenous solution was obtained. The solution was quickly placed in plastic straws with a 0.8 mm radius and placed in a freezer at  $-18^\circ C$ . The cryogellation reaction continued for 24 h under cryogenic conditions. The obtained cryogels were removed from the straws, cut into about 1 cm lengths, and washed with DI water for one day by placing them into a container, and the water was changed every 8 h for a total of three times. And finally, the prepared p(4-VP) cryogels were dried at  $40^\circ C$  and stored in an air tight container for further use.

### 2.3. Modification of p(4-VP) cryogels

P(4-VP) cryogels were modified by reacting with dibromo compounds with various alkyl chain lengths e.g., bare p(4-VP) cryogels

were reacted with 1,2 BE, 1,4 BB, 1,6 BH, and 1,8 BO in acetone at room temperature. In brief, for each modification reaction, 0.1 g bare p(4-VP) cryogels were used, and excess amounts of modification agent (at least 2-fold based on repeating unit of 4-VP in p(4-VP) cryogels) were added into 30 ml acetone in a container. The mixture was stirred for 15 h at room temperature at 500 rpm, and then the mixture was washed with excess acetone and filtered. Finally, the modified cryogels were dried at  $50^\circ C$  for 2 h, and stored in a closed container for later use.

### 2.4. In situ preparation of Co, Ni, Cu, and Fe nanoparticles within p(4-VP)-based cryogel

Different metal chloride salts such as Co, Ni, Cu, and Fe were loaded into cryogel from their corresponding alcohol solutions to determine the effect of metal species, and metal nanoparticles were prepared inside the cryogels as reported by our previous studies [2,25–27]. About 5 g 1,4 BB-p(4-VP) cryogels were placed into 500 ml of 1000 ppm metal ion solutions for 24 h until maximum loading of metal ions into the cryogels was accomplished as determined by AAS. The metal salt-loaded cryogels were washed with ethanol to remove unbound metal ions from the cryogel network and then dried at about  $50^\circ C$  for 2 h. To form metal nanoparticles within the modified p(4-VP) cryogel, metal salt-loaded p(4-VP) based cryogels were treated with 50 ml 0.2 M aqueous  $NaBH_4$  solution for 1 h for in situ reduction of metal ions to their corresponding metal nanoparticles. The metal nanoparticle-loaded cryogel composites were used as catalyst systems for the hydrolysis of  $NaBH_4$ , 4-NP reduction and MB degradation.

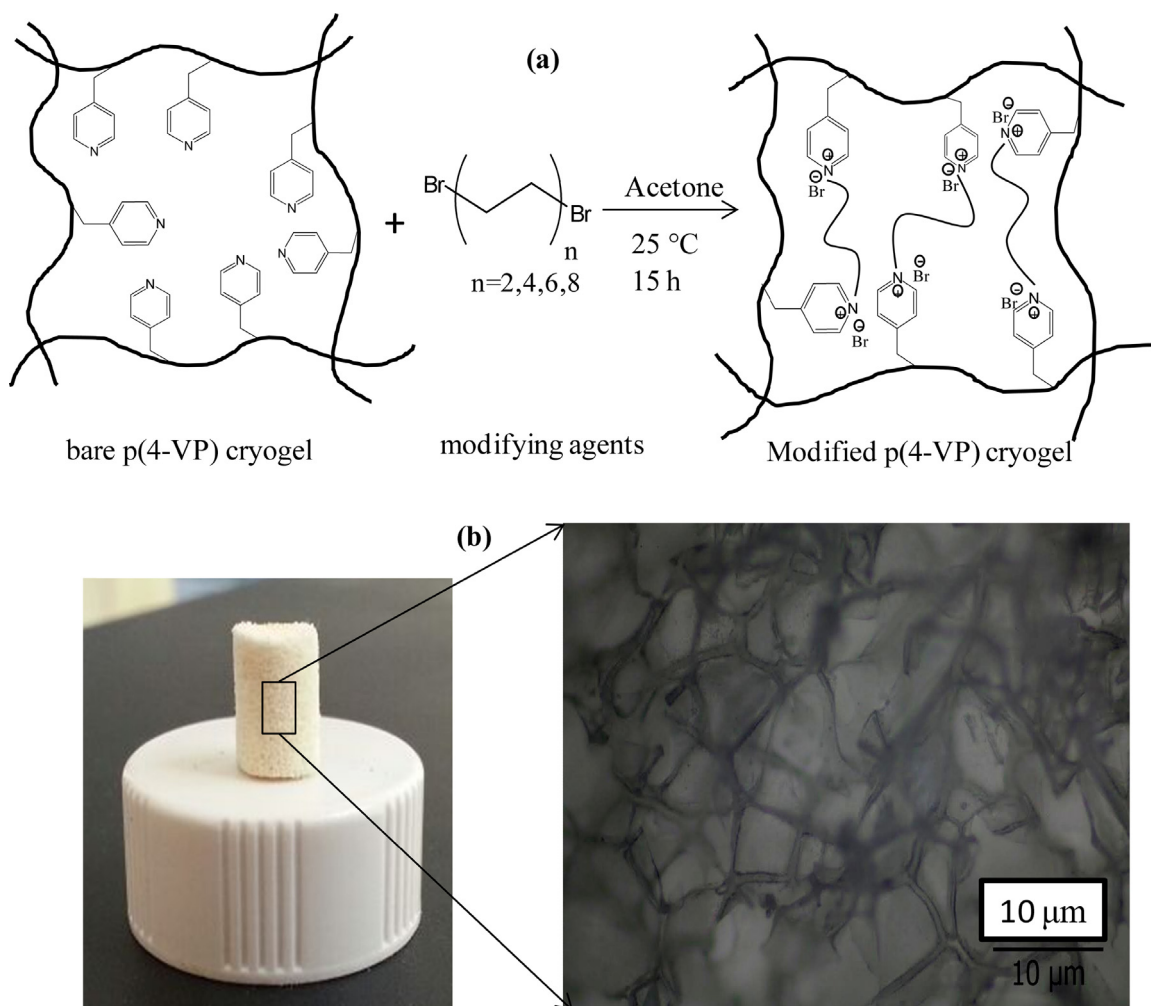
### 2.5. Characterization of 1,4 BB-p(4-VP) cryogels and its metal nanoparticle-containing composites

The quaternization peaks of p(4-VP) cryogels after reacting with various dibromoalkanes were determined using FT-IR spectroscopy (Thermo, Smart iTR) using ATR apparatus. The porous structure of 1,4 BB-p(4-VP) cryogels were readily visualized by optical microscopy (Olympus bX53). The thermal characterization of bare p(4-VP) cryogels, and 1,4 BB-p(4-VP) cryogels and its composites with metal nanoparticles was completed using a thermogravimetric analyzer (Seiko SII TG/DTA 6300). Approximately 5 mg bare p(4-VP), 1,4 BB-p(4-VP) and 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, and Fe) cryogels were placed in a ceramic pan, and the weight losses with increasing temperature were recorded. The TGA measurements were performed under  $N_2$  flow of  $100\text{ ml min}^{-1}$  with  $10^\circ C\text{ min}^{-1}$  temperature increments between 50 and  $1000^\circ C$ .

The amounts of metal ions within superporous cryogel composites were determined by Atomic Absorption Spectroscopy (AAS, Thermo, ICA 3500 AA SPECTRO). Bare p(4-VP) and 1,4 BB-p(4-VP)-M composite cryogels were treated with 30 ml 5 M HCl solution three times until the metal nanoparticles were dissolved from the cryogel matrices and the amounts of metal ions were determined by AAS measurement. The metal nanoparticles within 1,4 BB-p(4-VP) cryogels were imaged via TEM (JEOL 2010, Japan) in a vacuum with an operating voltage of 200 kV.

### 2.6. Hydrolysis of $NaBH_4$ catalyzed by 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, Fe) cryogel composites

In the hydrolysis of  $NaBH_4$  certain amounts of 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, Fe) cryogel composites containing equal amounts of Co, Ni, Cu, and Fe nanoparticles were placed into 50 ml water at  $30^\circ C$ . To initiate the hydrolysis reaction, 50 mM (0.0965 g)  $NaBH_4$  was added to this reaction mixture and stirred at 1000 rpm. The volume of generated  $H_2$  gas with time was measured in an experimental set up where the produced  $H_2$  gas replaced water in an



**Fig. 1.** (a) The schematic presentation of modification of p(4-VP) cryogels with dibromo alkanes containing different carbon numbers, and (b) digital camera image and optical microscope image of 1,4 BB modified dicationic p(4-VP) cryogels as 1,4-BB-p(4-VP).

inverted volumetric cylinder. All the experiments were repeated at least three times and results are given as the averages of these three measurements with their standard deviations.

The effect of metal nanoparticle species on hydrolysis of  $\text{NaBH}_4$  was determined by using p(4-VP)-M cryogel composites containing equal amounts (0.093 mmol) of Co, Ni, Cu, and Fe utilized as catalyst systems for the hydrolysis of  $\text{NaBH}_4$  under the same reaction conditions; that is 50 mM 50 ml aqueous  $\text{NaBH}_4$  solution, at 30 °C, and 1000 rpm mixing rate.

The amounts of metal nanoparticles within 1,4 BB-p(4-VP) cryogels was increased by multiple metal salt loading and reduction cycles, and the effect of multiple loading-reduction cycles of Co on the hydrolysis of  $\text{NaBH}_4$  was done by using 0.1 g 1,4 BB-p(4-VP) Co as catalyst system under the same conditions (50 mM 50 ml aqueous  $\text{NaBH}_4$  solution, at 30 °C, 1000 rpm). To determine the effect of temperature on  $\text{NaBH}_4$  hydrolysis and determine the activation parameters, 0.1 g 1,4 BB-p(4-VP)-Co cryogel composite was used in  $\text{NaBH}_4$  hydrolysis at 30, 50, 60, and 70 °C under the same reaction conditions.

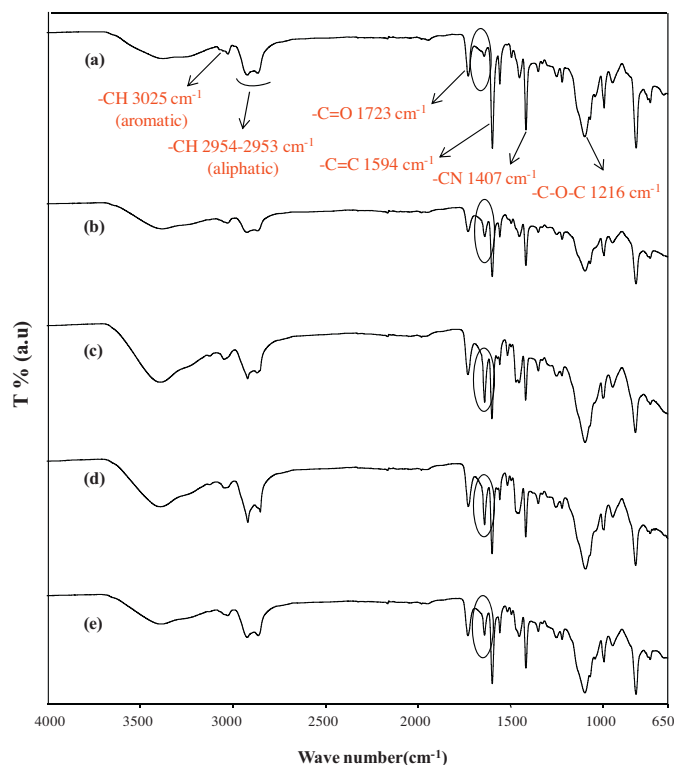
#### 2.7. Reduction of 4-NP to 4-AP by 1,4 BB-p(4-VP)-M composite cryogels

The reduction reaction of 0.01 M aqueous 4-NP to 4-AP was carried out in the presence of 50 ml 0.4 M  $\text{NaBH}_4$  by 0.1 g of

1,4 BB-p(4-VP)-M cryogels, including same amounts of Co, Ni, Cu, and Fe nanoparticles, placed into the reaction solution to initiate the reduction of nitro compounds to 4-AP. During the reduction reaction, 0.1 ml samples were taken from the medium, and diluted 80 times with DI water. The conversion of 4-NP to 4-AP due to the reduction process and reaction rate was determined by measuring the change in intensity of UV-vis spectra at 400 nm of the solution according to a previously constructed calibration curve. There was also a peak at 290 nm with gradual increase as the reduction reaction proceeds due to the formation of 4-AP.

#### 2.8. Catalytic degradation of methylene blue with 1,4 BB-p(4-VP)-Cu composites in different media

The catalytic degradation of MB, an organic dye, was done by employing 1,4 BB-p(4-VP)-Cu (0.0869 g Cu) and  $\text{NaBH}_4$  ( $2 \times 10^{-2}$  M, 100 ml). The concentration of MB was 100 ml  $0.4 \times 10^{-4}$  M. During catalytic degradation of MB, 1 ml samples were taken from the reaction flask at about 1 min intervals and diluted 3 fold. The degradation of MB was determined by measuring the change in intensity of UV-vis absorption spectra at 664 nm belonging to MB before degrading. The degradation reactions were carried out in DI water under 500 rpm mixing rate at 30 °C, unless otherwise stated.



**Fig. 2.** FT-IR spectra of (a) bare p(4-VP), (b) 1,2 BE-p(4-VP), (c) 1,4 BB-p(4-VP), (d) 1,6 BH-p(4-VP), and (e) 1,8 BO-p(4-VP).

### 3. Results and discussion

#### 3.1. Modification, characterization and determination of the amount of metal particles inside p(4-VP)-based cryogels

The schematic representation of p(4-VP) cryogels with various dibromoalkanes of different chain lengths is illustrated in Fig. 1(a). Different chain lengths of  $-(CH_2CH_2)_n-$  where  $n = 2, 4, 6, 8$  for 1,2-BE, 1,4-BB, 1,6-BH, and 1,8-BO were used as modifying agents. As shown, all the modifying agents generate cationic charge by reaction with pyridine nitrogen atoms of p(4-VP) cryogels. As shown in Fig. 1(b), the digital camera and optical image of modified 1,4 BB modified p(4-VP) cryogels as 1,4 BB-p(4-VP), pore dimensions are on the order of tens of micrometer in dry state. The characterization of modified p(4-VP)-based cryogels was confirmed with FT-IR spectrometry. As illustrated in Fig. 2, the bare p(4-VP) and modified p(4-VP) cryogels with various modification agents of different alkyl dihalides all have the same characteristic peaks in FT-IR spectra due to the quaternization of the pyridine rings. Also, the peaks at  $3025\text{ cm}^{-1}$  and  $2954\text{--}2923\text{ cm}^{-1}$  in the FT-IR spectrum of the p(4-VP) cryogels belong to aromatic and aliphatic C–H stretching frequency, at  $1594\text{ cm}^{-1}$  for C=C, and  $1407\text{ cm}^{-1}$  for C–N stretching frequency exist [2,26]. The peaks at about  $1723\text{ cm}^{-1}$  for C=O,  $1590\text{--}1550\text{ cm}^{-1}$  for C=C, and  $1216\text{ cm}^{-1}$  for C–O–C stretching from the crosslinker p(EGDA) [4], and the quaternization peaks at about  $1670\text{--}1630\text{ cm}^{-1}$  for all the bare p(4-VP) and modified p(4-VP) cryogels were observed and were in accordance with the literature [28]. In the literature microgels based on p(4-VP) have been synthesized in microemulsion and/or by free radical polymerization for different purposes as template for metal nanoparticle preparation such as Co, Ni, Cu, and Fe [25,26,29,30]. Here we prepared p(4-VP) and modified with 1,4 BB to load metal salts into the cryogels and reduced in situ to their corresponding metal nanoparticles, then used the prepared 1,4 BB-p(4-VP)-M (Co, Ni, Cu, and Fe) composites as catalyst for  $H_2$  generation from hydrolysis of  $NaBH_4$ .

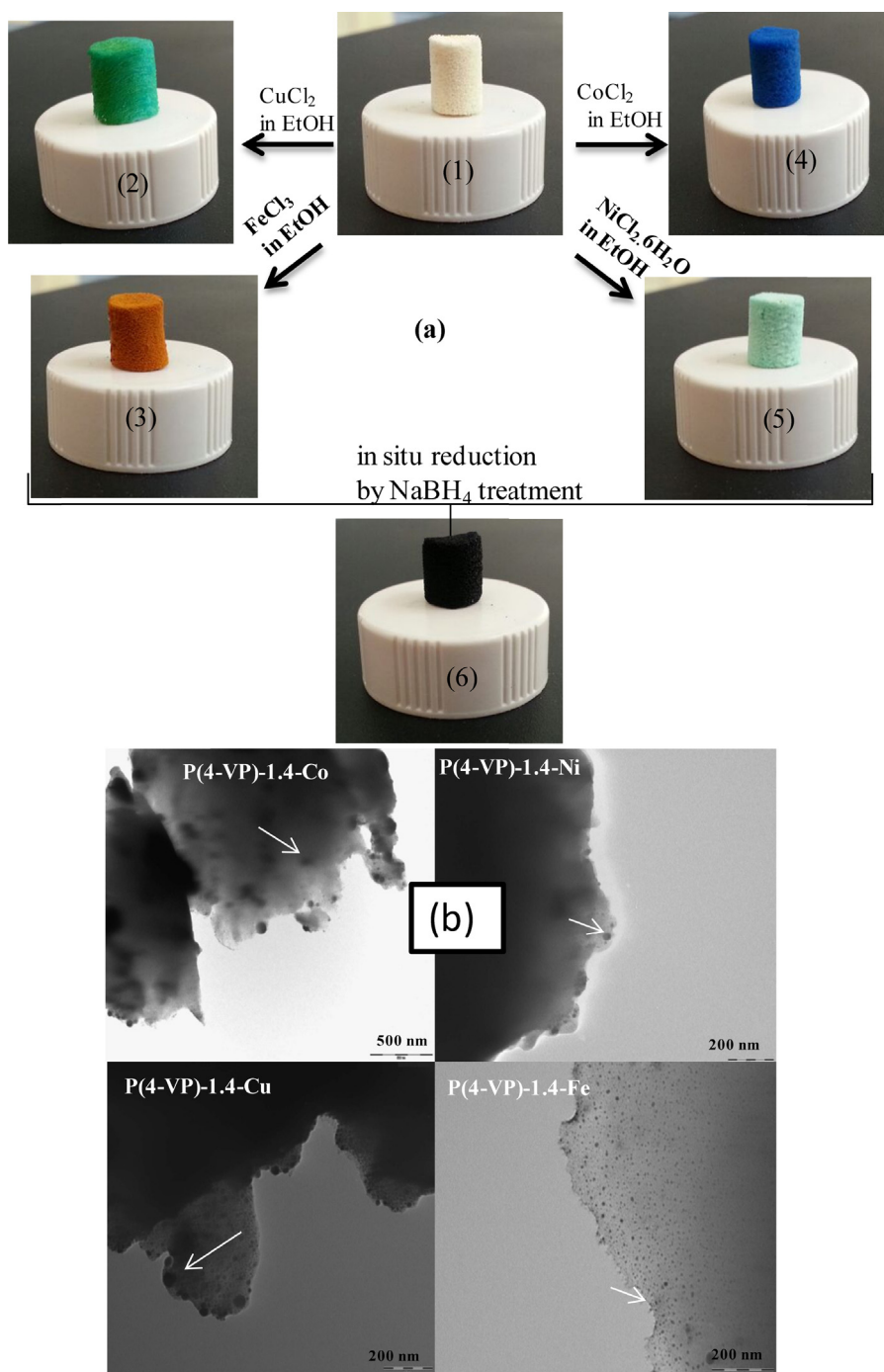
As shown in digital camera images in Fig. 3(a), the color of 1,4 BB-p(4-VP) cryogel were different after absorption into the cryogel network from ethanol of metal salts, depending on the types of metal salt. Upon treatment with  $NaBH_4$  of different metal salts within the cryogel matrices, the black color, as shown in (6) of in Fig. 3(a), is due to in situ formation of metal nanoparticles observed for all the cryogels with different metals. As illustrated in Fig. 3(b) in the TEM images for 1,4 BB-p(4-VP)-Co, 1,4 BB-p(4-VP)-Ni, 1,4 BB-p(4-VP)-Cu, 1,4 BB-p(4-VP)-Fe composites, the metal nanoparticles are distributed throughout the cryogel matrices. The size of metal nanoparticles within 1,4 BB-p(4-VP) cryogels was about 20–100 nm regardless of their origin.

The thermal stability and the amount of metal nanoparticles within cryogels were determined with TGA measurements by comparing the thermograms of bare 1,4 BB-p(4-VP) and 1,4 BB-p(4-VP)-M. TGA analysis was performed on bare p(4-VP), 1,4 BB-p(4-VP), 1,4 BB-p(4-VP)-Co, 1,4 BB-p(4-VP)-Ni, 1,4 BB-p(4-VP)-Cu and 1,4 BB-p(4-VP)-Fe cryogels as given in Fig. 4. The onset degradation of bare p(4-VP) cryogels was at about  $287^\circ\text{C}$  with 1.6% wt loss and then a sharp degradation between about  $287^\circ\text{C}$  and about  $425^\circ\text{C}$ , and then almost no degradation up to  $600^\circ\text{C}$  with 95.1% wt loss. The modified cryogel, 1,4 BB-p(4-VP), starts to degrade earlier than the bare p(4-VP) cryogels at about  $257^\circ\text{C}$  (by losing 2.8 wt %) and continues up to  $500^\circ\text{C}$  with dual sharp degradations. At about  $376^\circ\text{C}$ , 1,4 BB-p(4-VP) loss is 81 wt %, at about  $461^\circ\text{C}$  89.8 wt % is lost and up to  $600^\circ\text{C}$  almost no further degradation was observed. The thermograms of 1,4 BB-p(4-VP)-M cryogel composites revealed that their degradation profile is more or less similar to 1,4 BB-p(4-VP) cryogels, as shown in Fig. 4, but with lesser amounts of degradation up to  $600^\circ\text{C}$  due to their metal nanoparticle content. The wt % remaining for 1,4 BB-p(4-VP)-Fe, 1,4 BB-p(4-VP)-Cu, 1,4 BB-p(4-VP)-Co, and 1,4 BB-p(4-VP)-Ni cryogels were determined about 68, 39.5, 34, and 27, respectively. In order to determine the exact amount of metal content of 1,4 BB-p(4-VP)-M cryogels, they were treated with 30 ml 5 M HCl solution three times for 15 h repeatedly, then diluted a hundred fold (1/100) with DI water [31]. The amounts of metal ions were measured with AAS, and the results are given in Table 1. The amounts of metal nanoparticles within p(4-VP)-Co, 1,4 BB-p(4-VP)-Co, 1,4 BB-p(4-VP)-Ni, 1,4 BB-p(4-VP)-Cu, and 1,4 BB-p(4-VP)-Fe cryogels were determined as  $65.5 \pm 1.8$ ,  $54.5 \pm 4.5$ ,  $40.6 \pm 4.4$ ,  $67.7 \pm 0.5$ , and  $68.0 \pm 1.6\text{ mg/g}$ , respectively. To increase the amount of metal nanoparticles, and increase the catalytic reaction rates which are generally directly related to the amount of catalyst (metal nanoparticles), 1,4 BB-p(4-VP) cryogels were exposed to several metal salt loading and reduction cycles where 1,4 BB-p(4-VP) cryogels were placed in Co salt solution in ethanol, and reduced with  $NaBH_4$  for 1st time 1,4 BB-p(4-VP)-Co cryogel composites, and then after washing with ethanol this composite was again loaded with Co salt and then reduced with  $NaBH_4$  treatment for a 2nd time, and similar steps were followed for the 3rd time. The amount of Co particles loaded after the first loading-reduction cycle is low,  $54.5 \pm 4.5\text{ mg/g}$ , and this amount increased to  $109.4 \pm 17.8\text{ mg/g}$  after the third loading-reduction cycle.

#### 3.2. The effect of modification of p(4-VP) cryogels, NaOH and metal species on $H_2$ production by hydrolysis of $NaBH_4$

The effect of chemical modification of p(4-VP) cryogels on  $NaBH_4$  hydrolysis reaction, as shown in Fig. 5(a), was demonstrated by performing the reaction using the same amounts of Co-containing bare p(4-VP)-Co and 1,4 BB-p(4-VP)-Co in the hydrolysis of 50 mM 50 ml aqueous  $NaBH_4$  solution at  $30^\circ\text{C}$  and 1000 rpm mixing rate. As can be seen, although the cryogels containing the same amounts of Co metal nanoparticles were used, the 1,4 BB-p(4-VP)-Co catalytic performance is better than un-modified

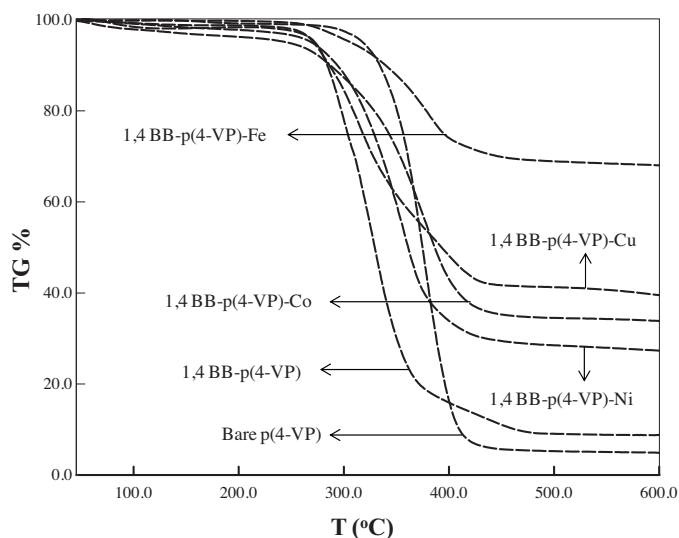




**Fig. 3.** (a) The digital camera images of (1) 1,4 BB-p(4-VP) cryogel, (2) 1,4 BB-p(4-VP)-Cu cryogel, (3) 1,4 BB-p(4-VP)-Fe cryogel, (4) 1,4 BB-p(4-VP)-Co cryogel, (5) 1,4 BB-p(4-VP)-Ni cryogel, and (6) their reduced forms as 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, Fe) cryogel composites, and (b) TEM images of 1,4 BB-p(4-VP)-Co, 1,4 BB-p(4-VP)-Ni, 1,4 BB-p(4-VP) Cu, and 1,4 BB-p(4-VP) Fe cryogel composites.

p(4-VP)-Co cryogel catalyst composites. Even though the amount of produced  $\text{H}_2$  is the same under the same reaction conditions, the time for the production of about 250 ml is faster for the modified cryogel, 1,4 BB-p(4-VP)-Co, at about 30.5 min, whereas the same amount of  $\text{H}_2$  was produced by p(4-VP)-Co cryogel in about 86 min. Therefore, it is obvious that the chemical modification definitely has a significant effect on hydrogen production rates. The effect of metal species on  $\text{H}_2$  production from the hydrolysis of  $\text{NaBH}_4$  is demonstrated in Fig. 5(b) by carrying out the same hydrolysis reaction of  $\text{NaBH}_4$  (50 mM 50 ml aqueous  $\text{NaBH}_4$  solution containing 5 wt % NaOH at  $30^\circ\text{C}$  and 1000 rpm mixing rate) with 1,4

BB-p(4-VP)-M (M: Co, Ni, Cu, Fe) containing the same amounts of metal nanoparticles (M: 0.093 mmol). As illustrated in Fig. 5(b), 250 ml  $\text{H}_2$  gas was generated with 1,4 BB-p(4-VP)-M (M: Co, Ni), and the time to produce this much  $\text{H}_2$  was 51 min for Ni, 55.5 min for Co cryogels, and there was no  $\text{H}_2$  production by Cu, and for Fe-containing 1,4 BB-p(4-VP) cryogels. Cu cannot catalyze  $\text{NaBH}_4$  hydrolysis, whereas Fe can catalyze  $\text{NaBH}_4$  hydrolysis only in the absence of NaOH. Therefore, as illustrated in Fig. 5(b), the hydrolysis reactions were carried out in the presence of NaOH, therefore there were no  $\text{H}_2$  production in  $\text{NaBH}_4$  hydrolysis catalyzed by and 1,4 BB-p(4-VP)-Fe and 1,4 BB-p(4-VP)-Cu cryogel composites. Due



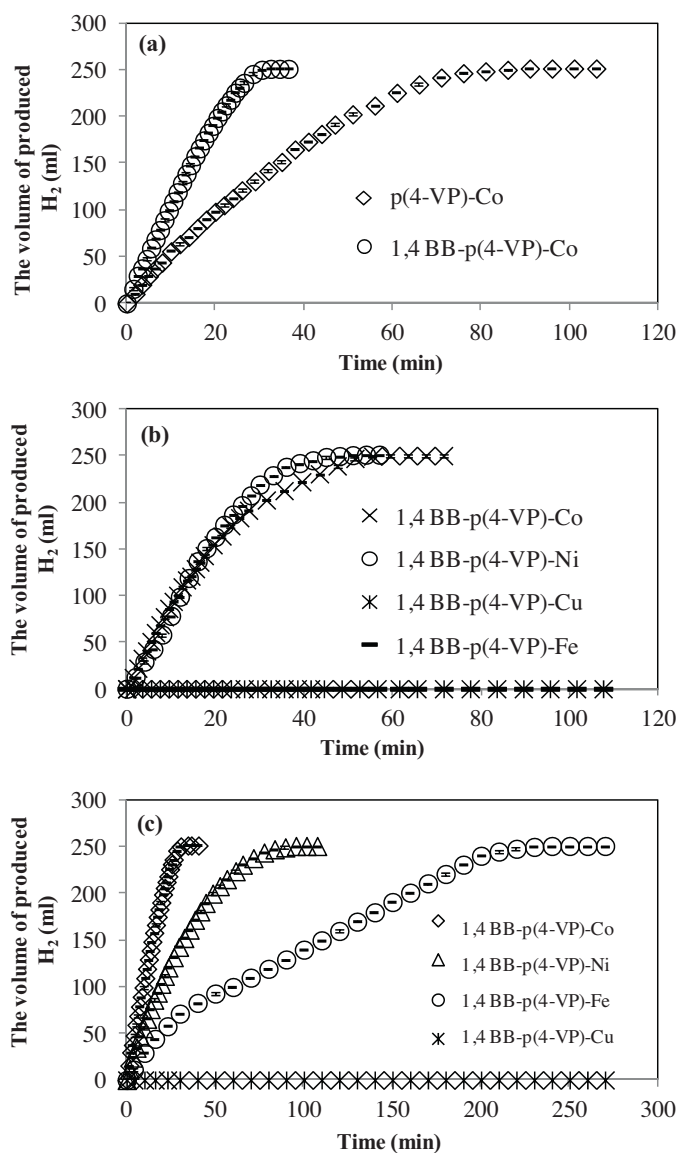
**Fig. 4.** Thermogram of bare p(4-VP) cryogel, 1,4 BB-p(4-VP), and 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, and Fe) cryogel composites. The non-degrading wt % was 68 wt % for Fe, 39.5 wt % for Cu, 34 wt % for Co, and 27.4 wt % for Ni.

**Table 1**

The amount of metal nanoparticles within 1,4 BB-p(4-VP)-(M: Co, Ni, Cu and Fe) cryogel composite catalysts measured with AAS.

Cryogel composite catalysts	AAS (mg/g)
p(4-VP)-Co	67.5 ± 1.8
1,4 BB-p(4-VP)-Co 1st loading	54.5 ± 4.5
1,4 BB-p(4-VP)-Ni	40.6 ± 4.4
1,4 BB-p(4-VP)-Cu	67.7 ± 0.5
1,4 BB-p(4-VP)-Fe	68.0 ± 1.6
1,4 BB-p(4-VP)-Co 2nd loading	65.1 ± 11.0
1,4 BB-p(4-VP)-Co 3rd loading	109.4 ± 17.8

to the excess amount of  $\text{OH}^-$  ions in the reaction medium, Fe particles are converted to inactive  $\text{Fe}(\text{OH})_3$  that cannot catalyze  $\text{NaBH}_4$  hydrolysis [38]. However, as will be shown Fig. 5(c), and onward (in Table 2), the hydrolysis of  $\text{NaBH}_4$  can be catalyzed by 1,4 BB-p(4-VP)-Fe cryogel composite for  $\text{H}_2$  generation in the absence of NaOH, and the characteristic parameters for  $\text{NaBH}_4$  hydrolysis in absence of NaOH is given in Table 2. So, amongst 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, and Fe) composites, the Ni-containing modified cryogel provided faster  $\text{H}_2$  generation time. On the other hand, the same hydrolysis reactions were carried out without the use of NaOH, and better activity was obtained for 1,4 BB-p(4-VP)-Co composite cryogels than 1,4 BB-p(4-VP)-Ni composite cryogels as demonstrated in Fig. 5(c). Interestingly, although 1,4 BB-p(4-VP)-Cu and 1,4 BB-p(4-VP)-Fe cryogel composites cannot generate any  $\text{H}_2$  in the presence of NaOH in the  $\text{NaBH}_4$  hydrolysis, 1,4 BB-p(4-VP)-Fe can catalyze  $\text{NaBH}_4$  hydrolysis at a much slower rate in comparison to Co- and



**Fig. 5.** (a) The effect of chemical modification of p(4-VP) cryogels on hydrolysis reaction of  $\text{NaBH}_4$ , and (b) the effect of metal species on hydrolysis reaction of  $\text{NaBH}_4$  by 1,4 BB-p(4-VP)-M cryogel composites [M: Co, Ni, Cu, and Fe each 0.093 mmol, 50 mM 50 ml aqueous  $\text{NaBH}_4$  solution including 5 wt % NaOH, at 30 °C, 1000 rpm], and (c) in the absence of NaOH.

Ni-containing modified cryogels. Again, interestingly, 1,4 BB-p(4-VP)-Co cryogel catalyst system produced  $\text{H}_2$  much faster than 1,4 BB-p(4-VP)-Ni cryogel when there was no NaOH in the hydrolysis medium of  $\text{NaBH}_4$ . In  $\text{NaBH}_4$  hydrolysis, general NaOH is added in

**Table 2**

The comparison of HGR and TOF values for the hydrolysis of  $\text{NaBH}_4$  by various cryogel composite catalyst systems.

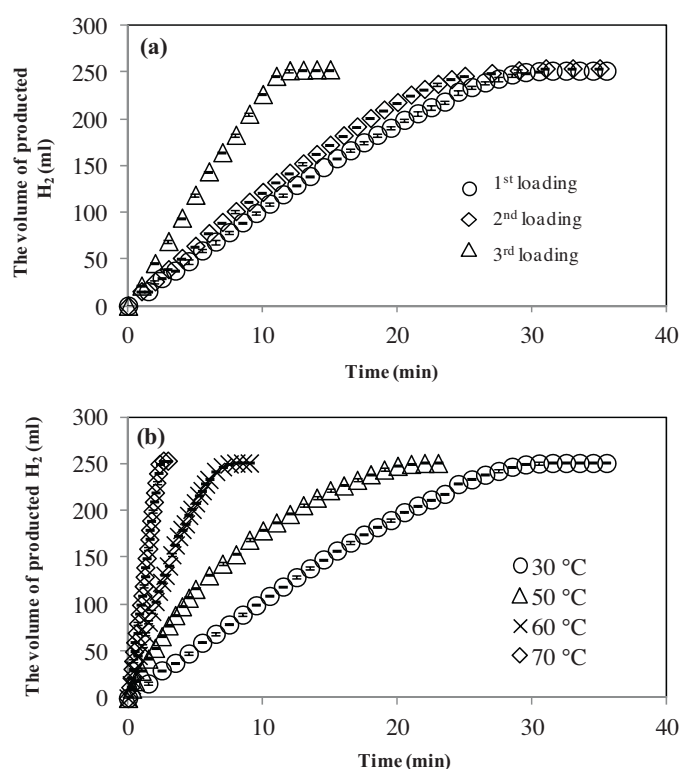
p(4-VP)-M (M: Co, Ni, Cu, Fe) based composite	T (°C)	Metal content (mmol)	Hydrogen generation rates (ml $\text{H}_2$ ) (g of Co min) $^{-1}$	Total turn over frequency, TOF (mol $\text{H}_2$ ) (mol catalyst min) $^{-1}$
1,4 BB-p(4-VP)-Ni	30	0.093	650 ± 71.0	1.5 ± 0.2
1,4 BB-p(4-VP)-Cu	30	0.093	-	-
1,4 BB-p(4-VP)-Fe	30	0.093	234 ± 6.0	0.6 ± 0.1
Bare p(4-VP)-Co	30	0.093	681 ± 18.0	1.6 ± 0.1
1,4 BB-p(4-VP)-Co 1st loading	30	0.093	1693 ± 290.0	3.9 ± 0.3
1,4 BB-p(4-VP)-Co	50	0.093	2603 ± 216.0	5.8 ± 0.5
1,4 BB-p(4-VP)-Co	60	0.093	7573 ± 630.0	16.4 ± 1.2
1,4 BB-p(4-VP)-Co	70	0.093	20,411 ± 1690.0	42.8 ± 3.6
1,4 BB-p(4-VP)-Co 2nd loading	30	0.111	1708 ± 142.0	4.1 ± 0.5
1,4 BB-p(4-VP)-Co 3rd loading	30	0.186	2112 ± 348.0	5.0 ± 0.8

the medium to prevent self-hydrolysis [10]. It is known that  $\text{NaBH}_4$  is  $\text{Na}^+$  and  $\text{BH}_4^-$  in aqueous solutions, and upon modification with 1,4-BB, the p(4-VP) cryogels become positively charged (1,4 BB-p(4-VP)), and the presence of  $\text{OH}^-$  in the reaction medium prevent the absorption of  $\text{BH}_4^-$  ions on and into cryogels network where the catalytic reaction takes places. Therefore, without NaOH, 1,4 BB-p(4-VP)-Co containing cryogels provide better catalytic activities toward  $\text{H}_2$  production [2,25,30]. Keep in mind that in all the hydrolysis reactions, the amount of M was equal, 0.093 mmol (M: Co, Ni, Cu, and Fe) in the cryogels. As illustrated in Fig. 5(c), 250 ml  $\text{H}_2$  gas was generated with 1,4 BB-p(4-VP)-Co cryogels in 32.5 min, whereas the same amount of  $\text{H}_2$  gas was produced with 1,4 BB-p(4-VP)-Ni cryogels in about 101.5 min, it took about 250 min for 1,4 BB-p(4-VP)-Fe, and no  $\text{H}_2$  was generated by p(4-VP)-Cu. Accordingly, without the use of NaOH in the hydrolysis of  $\text{NaBH}_4$ , the order of the composite catalyst for 1,4 BB-p(4-VP)-M cryogel composite system is  $\text{Co} > \text{Ni} > \text{Fe} >$ .

The other catalytic parameters of 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, Fe) cryogel composite catalyst systems, such as turn over frequencies (TOF), and hydrogen generation rates (HGR), were calculated and are given in Table 2. As can be seen the TOF value for 1,4 BB-p(4-VP)-Co was calculated as  $3.9 \pm 0.3 \text{ mol H}_2 (\text{mol metal min})^{-1}$ , and for 1,4 BB-p(4-VP)-Ni it was  $1.5 \pm 0.2 \text{ mol H}_2 (\text{mol metal min})^{-1}$ , and for 1,4 BB-p(4-VP)-Fe it was  $0.6 \pm 0.1 \text{ mol H}_2 (\text{mol metal min})^{-1}$ . The HGR values for Co, Ni, and Fe-containing composite catalyst systems were calculated as  $1693 \pm 290 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$ ,  $650 \pm 71 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Ni})^{-1}$ , and  $234 \pm 6.0 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Fe})^{-1}$  respectively; again affirming the better catalytic performance of Co-containing composite catalyst systems [28,32].

### 3.3. The effect of metal reloading and reduction cycles of 1,4 BB-p(4-VP) cryogels, and reaction temperature on $\text{H}_2$ production rate from $\text{NaBH}_4$ hydrolysis

It is known that the catalyst amount has a direct effect on catalytic reaction rates. Hence, to determine the effect of Co amounts on  $\text{H}_2$  generation from the hydrolysis of  $\text{NaBH}_4$ , the amounts of Co metal nanoparticles in the cryogels were increased by multiple loading-reduction cycles of Co salts into 1,4 BB-p(4-VP) cryogels, and they were used in the hydrolysis of  $\text{NaBH}_4$ . To support the idea that the increase in the amount of catalyst increases the reaction rate is based on the assumption that for the certain concentration of molecules, the number of active sites for a catalyst are increased in a given reactor volume by increasing the amounts of catalyst. So, the molecules can readily meet with the active sites of the catalyst without too much struggle e.g., there will be less compete with each other, and the reaction rate will increase [28,32]. The amounts of Co metal nanoparticles in 0.1 g 1,4 BB-p(4-VP) cryogels were 0.093, 0.111, and 0.186 mmol Co for 1st, 2nd, and 3rd loading-reduction cycles that were all used in the hydrolysis of 50 mM 50 ml aqueous  $\text{NaBH}_4$  solution at 30 °C. As illustrated in Fig. 6(a), the graph of produced amount of  $\text{H}_2$  versus time for every Co salt loading and reduction cycle was constructed and each one produced 250 ml  $\text{H}_2$  at different times. As shown in the figure, the 1st time metal-loaded-reduced cryogels produced 250 ml  $\text{H}_2$  in 32.5 min, whereas the 2nd, and 3rd time metal-loaded and reduced cryogel composites generated the same amount of  $\text{H}_2$  in about 29 and 14 min, respectively. The TOF and HGR values for the 2nd and 3rd time loaded and reduced cycles of 1,4 BB-p(4-VP)-Co were calculated as  $4.1 \pm 0.5$  and  $5.0 \pm 0.8 \text{ mol H}_2 (\text{mol Co min})^{-1}$ , and  $1708 \pm 142$  and  $2112 \pm 348 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$ , respectively. It is clear that with the increase in the amounts of Co nanoparticles generated by multiple loading and reduction cycles of 1,4 BB-p(4-VP) cryogels, the TOF and HGR also increased. So, the template, p(4-VP) is resourceful because of chemical modification and higher amounts of metal



**Fig. 6.** The effects of (a) multiple Co salt loading and reduction cycles (the amount of Co metal nanoparticle) on  $\text{NaBH}_4$  hydrolysis at 30 °C, and (b) the hydrolysis reaction temperature on  $\text{NaBH}_4$  hydrolysis catalyzed by 1,4 BB-p(4-VP)-Co cryogel composites containing 0.093 mmol Co at 30, 40, 50, 70 °C [reaction conditions: 50 mM 50 ml  $\text{NaBH}_4$  solution, 1000 rpm].

nanoparticles can be loaded by multiple loading-reduction cycles of the desired metal salts.

To investigate the effect of temperature on  $\text{NaBH}_4$  hydrolysis, 0.1 g 1,4 BB-p(4-VP)-Co cryogels (containing 0.093 mmol Co) were utilized for the reaction carried out at 30, 50, 60, and 70 °C under the same reaction conditions. As illustrated in Fig. 6(b), upon the increase in the temperature from 30 to 70 °C, the hydrolysis reaction time decreases from 32.5 min to 2.6 min (increasing the reaction rate) for the  $\text{NaBH}_4$  hydrolysis reaction. As given in Table 2, the TOF and HGR values at 30, 50, 60, and 70 °C for  $\text{NaBH}_4$  hydrolysis reaction catalyzed by 1,4 BB-p(4-VP)-Co were  $3.9 \pm 0.3$ ,  $5.8 \pm 0.5$ ,  $16.4 \pm 1.2$ ,  $42.8 \pm 3.6 \text{ mol H}_2 (\text{mol Co min})^{-1}$  and  $1693 \pm 290$ ,  $7573 \pm 630$ ,  $20,411 \pm 1690 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$ , respectively. It is apparent that the increase in the hydrolysis reaction temperature increases the TOF and HGR values for the  $\text{NaBH}_4$  hydrolysis reaction. The comparison of these values with similar studies in the literature is given in Table 3, as can be seen the TOF and HGR values of 1,4 BB-p(4-VP)-Co cryogels offer advantages over p(4-VP)-Co cryogels<sup>2</sup> and microgels of p(4-VP)-Co composites [26]. The TOF and HGR for 1,4 BB-p(4-VP)-Co composite cryogels were  $3.9 \pm 0.3 \text{ mol H}_2 (\text{mol Co min})^{-1}$  and  $1693 \pm 290 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$ , whereas the same values for p(4-VP)-Co cryogels TOF were reported as  $2.1 \pm 0.4 \text{ mol H}_2 (\text{mol Co min})^{-1}$  and  $882 \pm 174 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$ , and similarly, the microgel p(4-VP)-Co composites' TOF and HGR values were reported as  $1.69 \text{ mol H}_2 (\text{mol Co min})^{-1}$  and  $735 (\text{ml H}_2) (\text{min})^{-1} (\text{g of Co})^{-1}$  [2,26]. It is evident that TOF and HGR values of 1,4 BB-p(4-VP)-Co composite cryogels are approximately 2 times more than p(4-VP)-Co cryogels and p(4-VP)-Co microgels. This is a significant difference and indicates the great advantage of 1,4 BB-p(4-VP)-Co cryogel catalyst systems in term of catalytic performances, ready preparation, economical effectiveness, and versatility for potential uses in real applications.

**Table 3**  
Comparison of the catalytic performances of Co nanoparticle-containing 1,4 BB-p(4-VP)-Co cryogels with p(4-VP) cryogels and p(4-VP) microgels for H<sub>2</sub> generation from the hydrolysis of NaBH<sub>4</sub>.

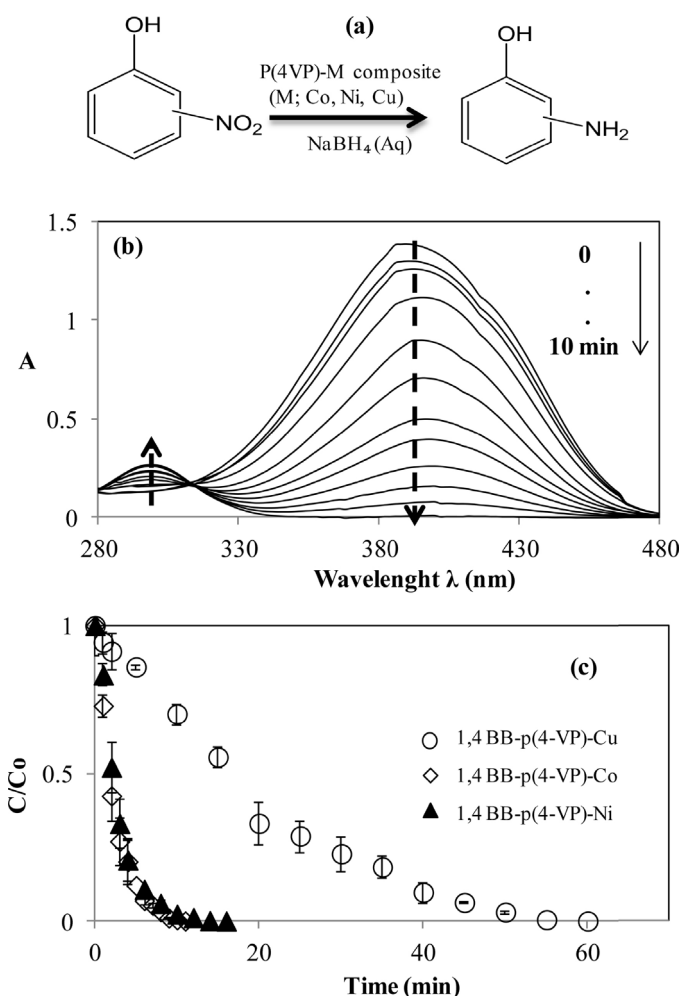
Parameters	1,4 BB-p(4-VP)-Co cryogel	P(4-VP)-Co cryogel [2]	P(4-VP)-Co microgel [26]
HGR (Hydrogen generation rate) (ml H <sub>2</sub> )/(g of Co) (min)	1693 ± 290.0	882 ± 174 <sup>a</sup>	735.0 <sup>a</sup>
TOF (Total turn over frequency) (mol H <sub>2</sub> )/(mol catalyst) (min)	3.9 ± 0.3	2.1 ± 0.4 <sup>a</sup>	1.69 <sup>a</sup>

<sup>a</sup> Data calculated based on the p(4-VP) microgels reported in previous study [2,26].

The activation energies, enthalpy and entropy for NaBH<sub>4</sub> hydrolysis were calculated as 47.6 kJ (mol)<sup>-1</sup>, 46.2 kJ (mol K)<sup>-1</sup>, and -146.9 J (mol K)<sup>-1</sup>, respectively. There are reported literature *E<sub>a</sub>* values, some of which are higher, some of which are lower, than the *E<sub>a</sub>* value calculated [26,32].

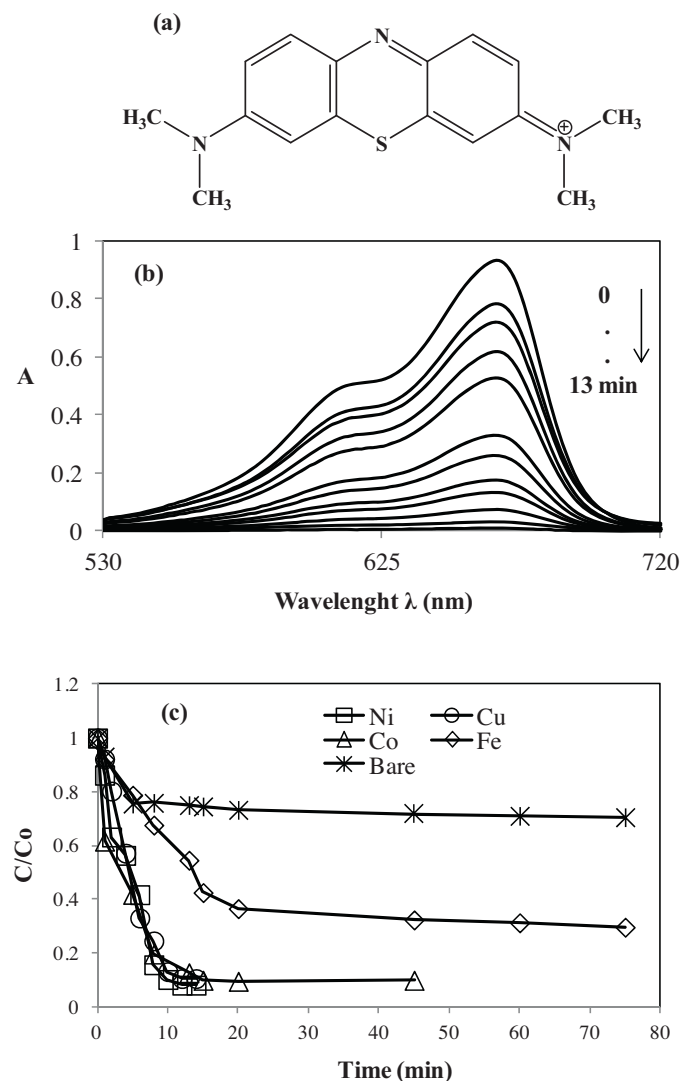
### 3.4. 4-nitrophenol reduction by 1,4 BB-p(4-VP)-M (Co, Ni, Cu) cryogel composite

As the reduction of some organic pollutants such as aromatic nitro compounds is very important due to environmental, agriculture, and industrial concerns [33], we tested the reduction capability of 1,4 BB-p(4-VP)-M cryogel composite. Fig. 7(a) illustrates the reduction reaction schema of 4-NP to 4-AP with the prepared cryogel composite catalytic system. The UV-vis spectrum



**Fig. 7.** (a) Schematic presentation of reduction of 4-NP to 4-AP (b) the UV-vis absorption spectra of 4-NP to 4-AP catalyzed by p(4-VP)-1,4 BB-Co composite particles, (c) the effect of metal species (M: Co, Ni and Cu) on 4-NP reduction to 4-AP [p(4-VP)-1,4 BB-M (M: Co, Ni, Cu = 0.093 mmol), 50 ml 0.01 M nitro compound solution, 0.4 M NaBH<sub>4</sub>, 30 °C, 800 rpm].

of the reduction for 4-NP at 30 °C by 1,4 BB-p(4-VP)-Co cryogel composite is illustrated in Fig. 7(b). As the reduction of 4-NP proceeds the intensity of the band at 400 nm decreases, whereas new band formation at about 290 nm due to the formation of 4-AP increases in accordance with the literature observations [34,35,38]. The mechanism of reduction of 4-NP to 4-AP is well studied even with variety of metal nanoparticles embedded in different environments including surfactants, silica, polymers and so on [10,34,35,38,12,39]. As a comparison of the catalytic activity of various metal nanoparticles, the reaction was completed with Co, Ni, and Cu embedded in the 1,4 BB-p(4-VP) cryogel network, using the same amount of



**Fig. 8.** (a) The chemical structure of MB, and (b) UV-vis spectra of degradation of MB by 1,4 BB-p(4-VP)-Cu composite, and (c) the effect of metal species on degradation of MB catalyzed by 1,4 BB-p(4-VP)-M composite cryogel (M: Co, Ni, Cu, and Fe) [Reaction conditions: 100 ml 0.4 × 10<sup>-4</sup> M MB, NaBH<sub>4</sub> = 2 × 10<sup>-2</sup> M, 30 °C with 500 rpm mixing rate using 0.093 mmol Cu in 1,4 BB-p(4-VP)-Cu or M in cryogel composites].



catalyst 0.093 mmol, under the same reaction conditions as demonstrated in Fig. 7(c). The composite cryogels of 1,4 BB-p(4-VP)-Co and 1,4 BB-p(4-VP)-Ni showed almost the same catalytic activity for 4-NP reduction reaction. However, the reduction rate constants of 4-NP by 1,4 BB-p(4-VP)-Cu catalyst system was much slower than Co- and Ni-nanoparticle containing cryogel systems. Therefore, it is clear that 1,4 BB-p(4-VP)-M cryogels can also be used in environmental applications for the reduction of toxic organic compounds as M could be a variety of metal nanoparticles that can also catalyze different reactions, e.g. for dehalogenation of some environmentally hazardous and aromatic materials [36,38,12,39].

### 3.5. Degradation of methylene blue with 1,4 BB-p(4-VP)-Cu cryogel composites

To show the versatility of the prepared cryogel composite catalyst systems a model dye MB, that causes serious environmental problems due to its toxicity and dark color, was used in a decolorization/degradation reaction catalyzed by 1,4 BB-p(4-VP)-Cu composites. It is known that copper nanoparticles have been utilized for the catalytic degradation of dyes [37], here we employed 1,4 BB-p(4-VP)-Cu cryogel composites in the decolorization/degradation of MB. The chemical structure of MB is illustrated in Fig. 8(a), and UV-vis spectra for the catalytic degradation of MB is given in Fig. 8(b). The decolorization/degradation reaction was carried out at 30 °C with 500 rpm mixing rate using 0.093 mmol Cu nanoparticles in 1,4 BB-p(4-VP)-Cu. As can be seen from the UV-vis spectra, the peak at about 665 nm which is the absorption maxima for MB completely disappeared in about 13 min as an indication of the catalysis by 1,4 BB-p(4-VP)-Cu cryogel composites. To determine of the catalytic performance of different metal nanoparticles for degradation of MB reaction, the reduction reaction was carried out in the presence of 1,4 BB-p(4-VP)-M (M: Co, Ni, Cu, and Fe) composite cryogels, utilizing the equal amount of catalyst, 0.093 mmol under the same reaction conditions;  $2 \times 10^{-2}$  M NaBH<sub>4</sub>,  $0.4 \times 10^{-4}$  M 100 ml MB, under 500 rpm mixing rate, and the results were illustrated in Fig. 8(c). As shown in Fig. 8(c), the degradation of MB is completed in 13 min by Cu and Ni containing 1,4 BB-p(4-VP)-M (M: Cu, Ni) cryogel composites, whereas it took 45 min to finish the degradation MB by the 1,4 BB-p(4-VP)-Co cryogel composites. On the other hand, only a small catalytic activity was observed by 1,4 BB-p(4-VP)-Fe cryogel composites, and no almost catalytic activity for bare 1,4 BB-p(4-VP) cryogel composites was observed as demonstrated in Fig. 8(c). Therefore, it was shown here that some dyes, organic pollutants, can also be degraded with modified p(4-VP)-M cryogels. And again, M could be any other metal nanoparticle in addition to Co, Ni, Cu, and Fe and they can catalyze the degradation or elimination of other organic compounds.

## 4. Conclusion

Here, we report multipurpose superporous p(4-VP) cryogel preparation and their modification with dibromo alkanes of various chain lengths. The chemically-modified super porous p(4-VP) cryogels were used as template for in situ metal nanoparticle preparation using Co, Ni, Cu and Fe by loading metal salts that are soluble in ethanol into the cryogels and then in situ reduction with NaBH<sub>4</sub> treatment. It was further demonstrated that 1,4 BB-p(4-VP)-M (M: Co, Ni, and Cu) cryogel composites are very useful as a green energy carrier for H<sub>2</sub> production from the NaBH<sub>4</sub> hydrolysis. And amongst the 1,4 BB-p(4-VP)-M catalyst systems, it was found that Co nanoparticle-containing 1,4 BB-p(4-VP) cryogel composite catalyzed the hydrolysis reactions faster than Ni and Fe without requiring any NaOH. It was also shown that the metal nanoparticle

content of 1,4 BB-p(4-VP) superporous cryogels can be increased by multiple metal salt loading and reduction cycles to attain better catalytic performances e.g., fast HGR of  $2112 \pm 348.0$  (ml H<sub>2</sub>) (min)<sup>-1</sup> (g of Co)<sup>-1</sup> from the hydrolysis of NaBH<sub>4</sub> was obtained by 3rd time Co salt loaded-reduced cryogel system versus  $1693 \pm 290.0$  (ml H<sub>2</sub>) (min)<sup>-1</sup> (g of Co)<sup>-1</sup> for 1st time Co salt loaded-reduced cryogel system. Moreover, the HGR and TOF values were found to be substantially temperature dependent e.g.  $20,411 \pm 1690.0$  (ml H<sub>2</sub>) (min)<sup>-1</sup> (g of Co)<sup>-1</sup> for HGR and  $42.8 \pm 3.6$  mol H<sub>2</sub> (mol Co min)<sup>-1</sup> for TOF value at 70 °C in comparison to  $1693 \pm 290.0$  (ml H<sub>2</sub>) (min)<sup>-1</sup> (g of Co)<sup>-1</sup> for HGR and  $3.9 \pm 0.3$  mol H<sub>2</sub> (mol Co min)<sup>-1</sup> for TOF value at 30 °C. A value of E<sub>a</sub>, 47.6 kJ (mol)<sup>-1</sup> comparable to the literature was obtained for 1,4 BB-p(4-VP)-Co cryogel composite in NaBH<sub>4</sub> hydrolysis. The resourcefulness and the versatility of 1,4 BB-p(4-VP)-M cryogel composite catalyst systems was further demonstrated in the elimination of various organic pollutants such as aromatic nitro compounds i.e., the reduction of 4-NP to 4-AP and decolorization/degradation of aromatic organic pollutants such as MB. As demonstrated in this investigation, 1,4 BB-p(4-VP)-M cryogel composites can be easily prepared as environmentally eco friendly cryogel networks and utilized for various catalytic reactions. The prepared 1,4 BB-p(4-VP)-M cryogel composite catalyst systems may catalyze other organic reactions as M can be any other metal nanoparticle, such as Ag, Au, Ru etc., in addition to Co, Ni, Cu, and Fe.

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